

(21) Application No 9000475.5

(22) Date of filing 09.01.1990

(30) Priority data
(31) 01105 (32) 06.03.1989 (33) ES

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(51) INT CL³
C01B 7/04

(52) UK CL (Edition K)
C1A AK3C

(56) Documents cited
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(58) Field of search
UK CL (Edition J) C1A AK3C
INT CL⁴ C01B
Online database: WPI

(54) Recovery of chlorine from hydrogen chloride by means of a transport catalyst process

(57) The method comprises two stages:

- (1) passing a gaseous current of hydrogen chloride across a fluidized bed of copper oxides and sodium chloride deposited onto a suitable support, the reaction of the hydrogen chloride with the oxides to form a complex chloride taking place in a reactor (11); and
- (2) passing the chlorinated transport catalyst over a fluidized bed of transport catalyst which contains copper chloride and sodium, injecting a mixture of oxygen and nitrogen, carrying out the oxidizing reaction in a reactor (21) and liberating chlorine from the catalytic mass while the copper chloride is converted into copper oxide, extracting a continuous flow of transport catalyst which returns to the first stage. An absorption/separation system (47) using carbon tetrachloride recovers the chlorine give off in the reactor (21).

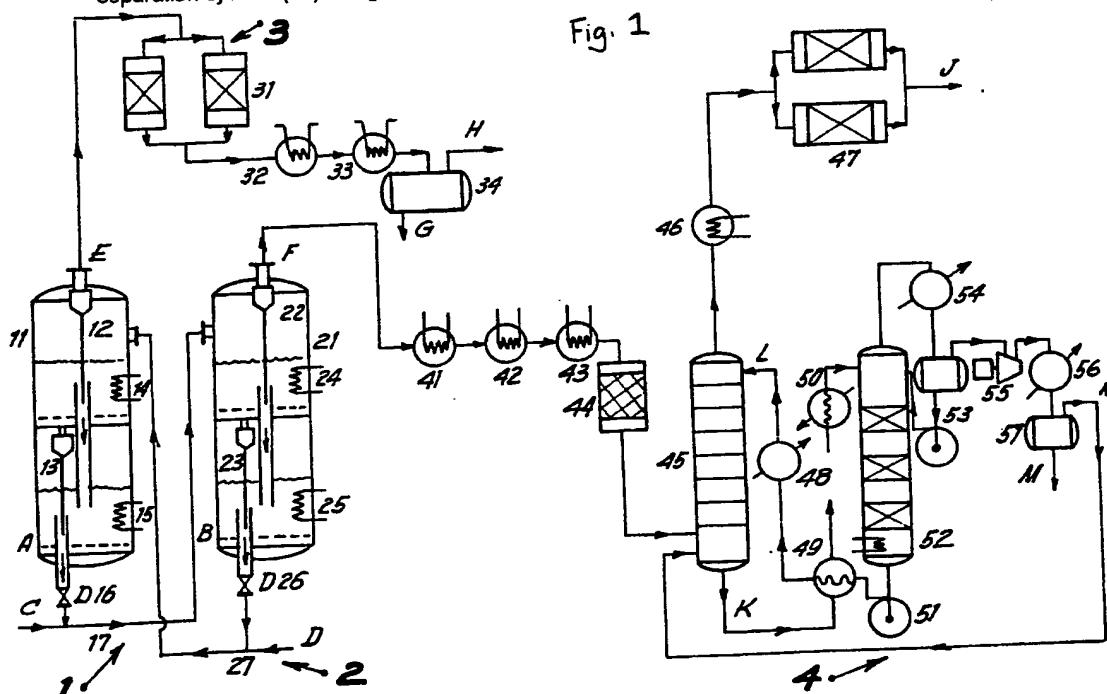
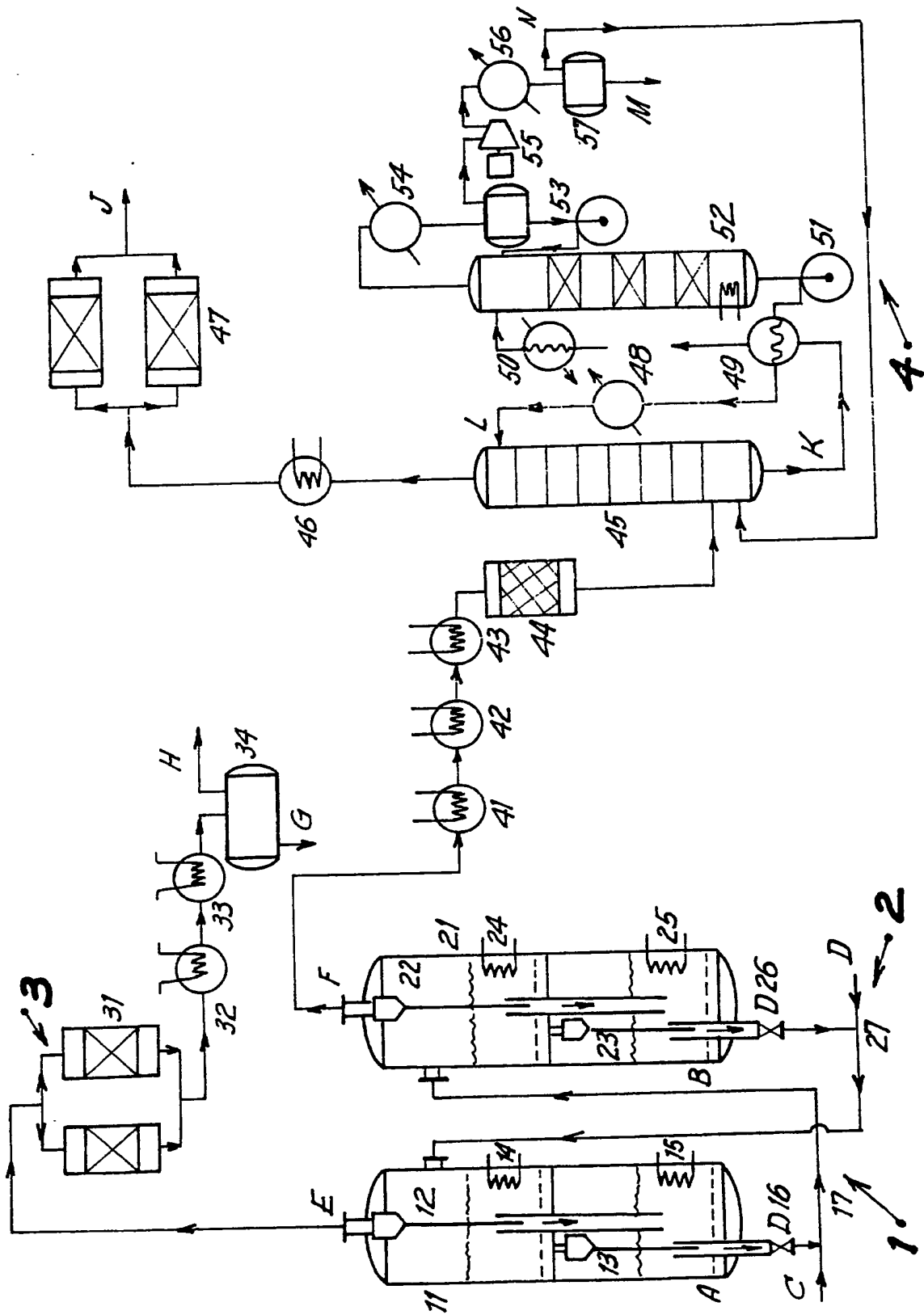


Fig. 1



METHOD FOR THE RECOVERY OF CHLORINE FROM
HYDROGEN CHLORIDE BY MEANS OF A TRANSPORT CATALYST
PROCESS AND EQUIPMENT FOR CARRYING OUT THIS METHOD.

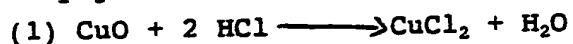
5 The present invention relates to a procedure for
the recovery of chlorine from hydrogen chloride, using a
transport catalyst. The equipment for carrying out this
procedure is also referred to.

10 Hydrogen chloride is obtained as a by-product in
many chemical processes, being recovered both in the
anhydrous gaseous form and in aqueous solution. Recovery
of the hydrogen chloride produced in chlorination
processes is necessary for ecological and environmental
15 reasons, but getting rid of this hydrogen chloride in an
economic manner has been a very difficult task which has
been studied for many years.

20 The procedure described in the present invention
makes use of a new technology the best definition of
which is that of a transport catalyst system. In the
previous attempts to recover chlorine from hydrogen
chloride catalytic systems formed by a metal or a group
of metals on an alumina or silica support have been
tried, with sufficient success but with considerable
25 problems. Among the problems which these methods present
is the extreme difficulty of separating the gases which
are given off from the catalytic reactor due to the
simultaneous presence in the gas current of hydrogen
chloride, chlorine, water, oxygen, nitrogen and other
products. In addition, it has been observed that the
30 catalyst used has, in general, a relatively short life
due to the fact that, in a chlorine atmosphere and at the
temperatures required for the reaction to proceed at an
economically suitable speed, the volatility of the metals
used is high.

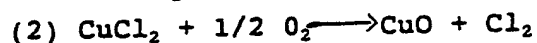
35 The procedure which is shown in the present
invention differs from the procedures which have already
been published in that it uses a transport catalyst

system. In the present technique the metals used to bring about the catalytic reaction are impregnated into a support mass, such as alumina, silica or a molecular sieve, which is suitable for use in the form of a fluidized bed. The first reaction is arranged so that it takes place in a sequence of stages which can be summarized by saying that they give rise to the following final result:



Stage 1: The gaseous current of hydrogen chloride, which is anhydrous or contains water and the hydrocarbons which may be present as impurities, crosses a fluidized bed of copper oxides and sodium chloride, deposited on a suitable support, which are in the molar ratio 1:1. The reaction takes place at a temperature of between 100 and 300°C. The hydrogen chloride reacts with the oxides to form a complex chloride, in accordance with the theoretical equation. The fluidized bed is maintained at constant temperature by means of a system of heat exchangers, arranged in the bed, which extract the heat of the exothermic reaction. In the preferred description of the procedure, the extracted heat is used to generate steam and in this manner improve the overall thermal balance of the procedure.

The chlorinated transport catalyst material is extracted continuously from the first chlorinating reactor and conducted to a second reactor, as is described below in stage 2.



Stage 2: The second reactor consists of a fluidized bed of transport catalyst which contains from 2 to about 20% of copper and sodium chlorides, which continuously mix with the current of similar material proceeding from the chlorinator. A mixture of oxygen and nitrogen, the oxygen content of which is between about 99% and about 10% by volume, is injected into the fluidized bed in this oxidizing reactor. The best temperature for the oxidation reaction is between 300 and 380°C. Under these conditions, oxidation takes place rapidly and free chlorine is liberated from the catalytic mass, while the

copper chloride is transformed into copper oxide.

A continuous flow of transport catalyst, which contains copper oxides, is extracted from the second reactor (the oxidizer) and returns to the first reactor (the chlorinator). A suitable heat exchange system is situated in the fluidized bed of the oxidizer and is used to raise the temperature to the appropriate level for the reaction velocity to be sufficiently high. The heat exchange system provides the heat for the endothermic reaction so as to maintain the transport catalyst system isothermic.

The above paragraphs describe the basic process under consideration. A flow diagram as shown in Fig.1 which illustrates the said process is included in this description of the invention.

There are many factors to be considered in this particular reaction system. The flow of gases which emerges from the chlorinator is essentially formed of water vapour together with the inert gases which can be present in the hydrogen chloride which initially took part. Basically in this stage chlorine is not liberated, and in consequence the gases which leave the reactor are easily condensed and removed without ecological risk.

With regard to the oxidizing reactor, the gases which leave the system at the maximum temperature are formed of free chlorine, unreacted oxygen and the nitrogen originally present. Depending on the manner in which the reaction is carried out, small quantities of water vapour can also be present in the gas. Nevertheless, recovery of the chlorine from this mixture is not complicated by the presence of hydrogen chloride, thus avoiding difficult problems of corrosion in the recovery train.

The complete flow throughout the process is represented in the flow diagram. As can be seen, the gases which leave the oxidation reactor pass through a heat exchanger and a heat recovery system in order to allow recovery of the high degree of heat which would be carried along by the hot gases.

This heat can be used to preheat the air and the oxygen which enter the oxidation reactor, or, in an alternative form, can be used to generate steam at high temperature and pressure, which can be used either in the process itself, or to generate electricity. Once the gas has been cooled by heat exchange to a suitable level, for example between 70-170°C, it is cooled still more with an air cooler in order to reduce the temperature to 40°C-50°C. The current of thus cooled gas, which contains the chlorine, is then directed into an absorption and separation system using carbon tetrachloride or another suitable solvent which absorbs the chlorine from the gas and concentrates it in the liquid phase used as absorption medium. The chlorine which is separated in this manner from the gas is liberated in a separation tower and afterwards is compressed, cooled, condensed and collected as liquid chlorine.

The nitrogen and the oxygen in the gas leaving the absorber are treated to separate the traces of chlorine which could be present, before proceeding to the chimney.

This system, as it has been described, has various advantages compared with other catalytic systems having a single stage which have been proposed in the prior art. These advantages are the following:

1. The conversion of hydrogen chloride to chlorine can take place in such a manner that it approximates to 100% in place of 80-83%, which is the conversion level attained by the previous systems described both in the literature and in the claims of patents.

2. The recovery of chlorine is simplified when the gas which contains it is free of hydrogen chloride, as in this case.

3. The gas which leaves the chlorinator is essentially free of hydrogen chloride and of chlorine, and basically consists of water vapour and inert gases which can be present in the starting hydrogen chloride. This simplifies the system which is needed for treating this

current of gas.

4. Due to the naturalness of the two stage process and the use of the transport catalyst to produce separation of the currents of chlorine and hydrogen chloride, the complete procedure is significantly less expensive than the alternative systems which had been considered. Table 1 shows an overall material balance for the procedure as it would be carried out. Table 2 gives an estimated cost of the said procedure for an installation capable of producing 30,000 tons/year of liquid chlorine from gaseous hydrogen chloride, showing the economic advantages of this approach compared with the similar procedures which have been described by others in the literature and patents.
5. The procedure, considered as a whole, uses an advanced system for the absorption of chlorine from the exit gases, thus materially reducing the magnitude of refrigeration and cold necessary for the final condensation of the chlorine.
6. Due to the fact that the products which leave the reactors are, in one case (chlorinator) principally water, and in the other case (oxidizer) simply chlorine in the presence of oxygen and nitrogen, the construction materials required for both reactors and the recovery system can be relatively less costly than they would need to be if the exit currents simultaneously contained chlorine and hydrogen chloride, as occurs in the alternative systems.
7. The use of a catalyst support allows the continuous recharging of the metallic material on the support, simply removing and replacing the transport catalyst while the procedure is working continuously. Experimental data have been gathered which show that this material retains a high degree of activity for periods of more than 10,000 to 20,000 hours of continuous work.

The typical supported catalyst system used for this process will contain copper chloride and sodium chloride in mol to mol proportions, placed on a support

of alumina, silica or molecular sieves. These materials must be selected such that they have a total surface area not less than values of between 200 and 500 square metres per gramme, having a pore diameter of between 40 and 100 angstrom. It has been shown that the copper chloride and the sodium chloride thus prepared form, at the working temperature, a melted mixture in the pore structure of the catalyst, which increases its capability of reacting rapidly both with the hydrogen chloride and with the oxygen according to the specific reaction which takes place in the reaction zone of the fluidized bed.

One method for the preparation of the catalyst used in this system is the following: copper chloride and sodium chloride, in the chosen suitable proportions and in saturated solutions, are mixed with the suitable support material. The proportions of the mixture are of an order of magnitude such that the final product will contain between 5 and about 20% of active copper material on the solid support. Once the material has been impregnated, it is dried at approximately 120 degrees and then calcined at 300 degrees C. Calcination takes place in a fluidized bed using preheated inert gas. As has been indicated above the solid support should be selected to have a particle size distribution suitable for fluidization in a normal fluidizing apparatus. Typical values for the particle size distribution are presented in Table 3. It should be emphasized that it is necessary to include a considerable fraction of small size material, with values of between 10 and 100 microns, to ensure that the catalyst has the desired fluid properties when it is stirred by a gas current with a superficial velocity of between 5 and 200 centimetres per second under the conditions existing in the interior of the reactor.

KEY TO THE FLOW DIAGRAM SHOWN IN FIG.1

- A. Feed hydrogen chloride.
- B. Gas containing oxygen.
- 5 C. Carrier gas for the chlorinated transport catalyst (normally steam).
- D. Carrier gas for the oxidized transport catalyst (normally steam).
- E. Gas emerging from the chlorinator, principally water vapour.
- 10 F. Gas emerging from the oxidizer, principally chlorine with nitrogen and oxygen.
- G. Condensate to be removed.
- H. Residual gas to be removed.
- J. Chlorine-free gas to the chimney.
- 15 K. Rich solution from the absorber.
- L. Poor solution to the absorber.
- M. Liquid chlorine product.
- N. Steam rich in chlorine to be recycled to the absorber.

1. CHLORINATOR

11. Chlorinator reactor (chamber formed of two parts separated by gratings.)
12. Internal cyclone.
5 13. Internal cyclone.
14. Absorption heat exchanger.
15. Heating resistances.
16. Regulating valve.
17. Tubing for transferring the catalyst carrier to the
10 oxidation reactor.

2. OXIDATION REACTOR

21. Oxidation reactor (chamber formed of two parts separated by gratings).
22. Internal cyclone.
15 23. Internal cyclone.
24. Heater.
25. Heater.
26. Regulating valve.
27. Tubing for transferring the catalyst carrier to the
20 chlorinator.

3. TREATMENT OF THE STREAM OF GASES FROM THE CHLORINATOR

31. Hydrogen chloride absorption bed.
32-33. Heat exchangers.

4. PURIFICATION OF THE CHLORINE WHICH EMERGES FROM THE OXIDATION REACTOR

- 41-42-43. Absorption heat exchanger.
44. Hydrogen chloride absorber bed.
30 45. Chlorine absorber.
46. Cooler for absorber.
47. Chlorine trap.
48. Cooler for regenerated absorbent.
49. Separator (decanter) of saturated from regenerated
35 absorbent.
50. Heater for chlorine-saturated absorbent.
51. Pump for recirculation of regenerated absorbent.
52. Fractionating column.
53. Reflux pump.

- 54. Reflux condenser.
- 55. Chlorine compressor.
- 56. Refrigeration plant (liquefier).
- 57. Chlorine chamber.

TABLE 1

Estimated material balance

- Bases: 1) Production of 100 metric tons per day
 2) Key letters referring to the flow diagram
 3) All quantities given in tons/day

Flow Number	Feed HCl	O ₂ (content in gas)	Gas emerging from the chlorinator	Gas emerging from the oxidizer	Condensor
KEY LETTER	A	B	E	F	G
Components:					
HCl	104	-	-	-	-
H ₂ O	15	-	42	-	42
O ₂	-	60	-	37	-
N ₂	-	12	-	12	-
Cl ₂	-	-	-	100	-
TOTALS	119	72	42 ^(a)	149 ^(b)	42 ^(c)

10

Flow Number Plant VENT CHLORINE (Production)

KEY LETTER	J	H
Components:		
HCl	-	-
H ₂ O	-	-
O ₂	37	-
N ₂	12	-
Cl ₂	-	100
TOTALS	49	100

Notes: a) May contain small quantities of HCl and O₂. b) May contain small quantities of H₂O.

c) The HCl present is removed by previous treatment.

TABLE 2

Cost comparison of the process

BASES: 30,000 metric tons per year of liquid chlorine production.

Economic data from published sources on HCl assuming the possibility of zero cost

Process	UHDE	KELCHLORO	SHELL	MTCHLOR	TRANSPORT
	ELECTROLYSIS			MITSUI	CATALYST
Capital Costs					
Million \$	16	13	12	11	9
Chemicals \$/Ton	2	6	4	4	4
Maintenance \$/Ton	50	30	25	22	20
Fixed Cost \$/Ton	80	65	60	55	45
TOTAL \$/TON	132	101	89	81	69

Notes: Chemicals include the catalyst cost, electrical power 0.06\$/kwh, steam at 6\$ per 1000 pounds.

TABLE 3

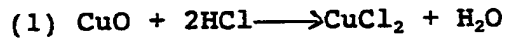
Particle size distribution in the transport catalyst process.

	Median particle size	40-80 (microns)
5	Surface area	200-700 m ² /g
	Pore size	40-200 Å (Ångstrom)
	PARTICLE SIZE (Microns)	PROPORTIONS BY WEIGHT (%)
	15-30	3-8
10	30-40	5-16
	40-50	12-22
	50-60	16-28
	60-80	10-26
	80-120	3-8

CLAIMS

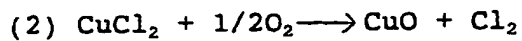
1. A method for the recovery of chlorine from hydrogen chloride by means of a transport catalyst process, which essentially comprises two stages:

- a first stage which consists in passing a gaseous current of hydrogen chloride which is anhydrous or contains water and the hydrocarbons which may be present, across a fluidized bed of copper oxides and sodium chloride, deposited on a suitable support, which are in the molar ratio 1:1, the reaction of the hydrogen chloride with the oxides taking place to form a complex chloride, according to the equation:



at a temperature of between 100 and 300°C, maintaining the fluidized bed at a constant temperature.

- a second stage which consists in passing the chlorinated transport catalyst material coming from the first stage across a fluidized bed of transport catalyst which contains from 2 to about 20% copper and sodium chloride, injecting a mixture of oxygen and nitrogen with an oxygen content of between about 99% and about 10% by volume, carrying out the oxidizing reaction at a temperature between 300 and 380°C, and liberating chlorine from the catalytic mass while the copper chloride is converted into copper oxide, according to the equation:



extracting from this second stage a continuous flow of transport catalyst which returns to the first stage.

2. Method according to claim 1, characterized in that the heat generated in the second oxidation stage is made use of in the first chlorination stage.

3. Method according to claim 1, characterized in that it comprises at least two contact stages in series in the first chlorination stage between hydrogen chloride gas and the transport catalyst, and in addition two contact stages in the second oxidation stage between the gas containing oxygen and the transport catalyst which has already absorbed the hydrogen chloride, thus ensuring the total conversion of the hydrogen chloride in the

first chlorination stage and more efficient utilization of the oxygen in the second oxidation stage.

4. Equipment for carrying out the procedure according to the above claims, characterized in that it comprises essentially at least two reactors, a first chlorinating reactor where the first chlorination stage takes place and a second oxidation reactor in which the second oxidation stage takes place, and a heat exchanger arranged in each of the fluidized beds of each reactor.

5. Equipment according to claim 4, characterized in that it comprises an absorption/separation system with carbon tetrachloride or other suitable solvent, for the recovery of the chlorine from the gases emerging from the oxidation reactor .

6. Equipment according to claims 4 and 5, characterized in that it comprises a gas turbine and an expansion chamber for using the heat generated in the chlorinating reactor as source of the energy necessary for the gas rich in oxygen to act as a fluidizer within the oxidation reactor .

7. Equipment according to claims 4 and 5, characterized in that it comprises internal cyclones placed such that the dust collected in the cyclone passes directly to the tubing for the exit of the solids at the bottom of the reactors ., thus minimizing the accumulation of fine dust in circulation within the reactor system.